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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAMSO-TR-77-248	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) NEW NUMERICAL METHODS APPLIED TO SOLVING THE ONE-DIMENSIONAL EIGENVALUE PROBLEM.		5. TYPE OF REPORT & PERIOD COVERED Interim rpt.
6. AUTHOR(s) Bernard R. Johnson		7. PERFORMING ORG. REPORT NUMBER TR-0078(3970-10)-1
8. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		9. CONTRACT OR GRANT NUMBER(s) F04701-77-C-0078
10. CONTROLLING OFFICE NAME AND ADDRESS Space and Missile Systems Organization Air Force Systems Command Los Angeles, Calif. 90009		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 14 November 1977
13. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		13. NUMBER OF PAGES 36p.
14. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		14. SECURITY CLASSIFICATION (of this Report) Unclassified
15. SUPPLEMENTARY NOTES		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. KEY WORDS (Continue on reverse side if necessary and identify by block number) Bound State Solution Eigenfunction Eigenvalue Numerical Methods Quantum Electronics		
17. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two new numerical methods, the log derivative and the renormalized Numerov, are developed and applied to the calculation of bound-state solutions of the one-dimensional Schrodinger equation. They are efficient and stable; no convergence difficulties are encountered with double minimum potentials. A useful interpolation formula for calculating eigenfunctions at nongrid points is also derived. Results of example calculations are presented and discussed.		

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I. INTRODUCTION

Numerical methods for obtaining bound-state solutions of the one-dimensional Schroedinger equation can be broadly classified into two types; numerical integration¹⁻⁶ (shooting methods) and matrix methods.⁶⁻¹³ The techniques to be described here belong to the integration category. They have been tested on a variety of problems and have proven to be efficient and trouble free in operation. They have several noteworthy features. They are very efficient of computer time (typical run times will be given in Section IV). No difficulties are encountered in converging to the desired solution in problems with double minimum potentials, even with a very high barrier between the minima. No overflow problems are encountered in the classically forbidden regions, so no special programming precautions have to be taken in this regard. Finally, the methods to be presented here can be easily and directly generalized to a practical method for calculating the eigenvalues and eigenfunctions of the multichannel Schroedinger equation.¹⁴

The calculation of eigenvalues will be discussed in Section II. The numerical techniques to be introduced are the log derivative and renormalized Numerov methods. The log derivative formulation has been discussed previously as a method for computing the S-matrix for scattering problems;¹⁵ the renormalized Numerov method is new. The calculation of eigenfunctions by the renormalized Numerov method will be discussed in Section III. Also, a very useful interpolation formula for calculating values of the eigenfunctions not located at the grid points will be derived. Finally, the results of example calculations and a general discussion will be presented in Section IV.

II. EIGENVALUE CALCULATIONS

The one-dimensional Schroedinger equation can be written in the form

$$\left[\frac{d^2}{dx^2} + Q(x) \right] \phi(x) = 0, \quad (1)$$

where

$$Q(x) = (2\mu/\hbar^2)[E - V(x)]. \quad (2)$$

The potential $V(x)$ is assumed to be capable of supporting one or more bound states. Acceptable bound state wavefunctions are required to be continuous together with their first derivatives, and must satisfy the boundary conditions

$$\phi(x) \xrightarrow{x \rightarrow \pm \infty} 0. \quad (3)$$

If Eq. (1) is a radial Schroedinger equation, the centrifugal potential is assumed to be included in $V(x)$ and the boundary condition at $=$ is replaced by

$$\phi(0) = 0. \quad (4)$$

The bound-state solutions of Eq. (1) have several well known properties. None of the energy levels of the discrete spectrum are degenerate. Also, if the eigenvalues are arranged in ascending order, then according to the oscillation theorem, the function $\phi_n(x)$ corresponding to the $(n+1)$ 'th eigenvalue E_n has n nodes.

It will be useful to begin the presentation by briefly outlining a commonly used integration method now in use so that it can be compared to our formulation. The x coordinate is divided into $N+1$ equally spaced

grid points from x_0 through x_N . The end points x_0 and x_N are located inside the classically forbidden regions on either side of the classically allowed region. A trial energy E is chosen, and Eq. (1) is integrated numerically. This solution is done in two parts, an outward integration starting at x_0 and an inward integration starting at x_N . They meet at a common matching point x_M located within the classically allowed region. The functions are normalized to $\psi(x_M) = 1$, and the difference in slopes at x_M is used to generate a correction ΔE , which is added to E to give an improved estimate of the eigenvalue. (For details see Refs. 1, 3 and 4.) This procedure is iterated and usually converges rapidly (quadratic convergence rate) to the eigenvalue E_n nearest in value to the initial guess.

A bisection procedure can be used initially to isolate, within a small energy interval, a single eigenvalue with a specified node count. Let us assume we know two energies E_L and E_H such that the desired eigenvalue lies between them

$$E_L < E_n < E_H. \quad (5)$$

Set the energy parameter in the Schrodinger equation equal to

$$E = 0.5(E_L + E_H), \quad (6)$$

then do the inward and outward integrations and count nodes. If the node count n_E is greater than n , set $E_H = E$, and, if lower, set $E_L = E$. If $n_E = n$, it is not possible to tell whether E lies above or below E_n by the node count. In this case calculate the second order correction ΔE . The sign of this correction is correct even if the magnitude is far off. If ΔE is negative, set $E_H = E$, and, if positive, set $E_L = E$. This procedure converges linearly and is iterated until E is close enough to E_n so that the quadratic converging method can be used. (For more details see Ref. 4.)

A. The Log Derivative Method

The method outlined above can be reformulated in terms of the logarithmic derivative of the wavefunction. In this section we describe a practical procedure to accomplish this.

The log derivative of the wavefunction is, by definition,

$$y(x) = \phi'(x)/\phi(x), \quad (7)$$

where the prime indicates differentiation with respect to x . It is easily verified that this function satisfies the Riccati equation

$$y'(x) + Q(x) + y^2(x) = 0. \quad (8)$$

From its definition, it is obvious that $y(x)$ has poles at the nodes of the wavefunction. Equation (8) is integrated outward from x_0 and inward from x_N to a common matching point x_M ($x_0 < x_M < x_N$). Since the outward integrated solution approaches x_M from the left, it will be designated by $y_l(x)$ and the inward integrated solution, which approaches from the right, by $y_r(x)$. The exact boundary conditions are given by Equations (3) and (4). In actual numerical calculations, the integration range usually does not extend from 0 to ∞ (or $-\infty$ to ∞). Rather, the points x_0 and x_N are located in the classically forbidden region on either side of the potential well and are far enough from the classical turning points so the calculated eigenvalues are insensitive to the initial values of the wavefunction at these points. Any error introduced by not using the correct value of the wavefunction at x_0 or x_N rapidly decays to insignificance as we integrate through the classically forbidden regions. For convenience, we have chosen to set $\phi(x_0) = \phi(x_N) = 0$. The derivatives must be $\phi'(x_0) \neq 0$ and $\phi'(x_N) \neq 0$, (or the wavefunction would vanish identically) but are otherwise arbitrary. The corresponding initial values for the log derivative function are $y_l(x_0) = \infty$ and $y_r(x_N) = -\infty$. Other authors^{2, 4} use the approximate W. K. B. solutions at x_0 and x_N . This choice will be discussed in

more detail at the end of the section. An exception to the method described above occurs in the case of s-wave bound states in an attractive potential well which has no short range repulsion. In this case there is no classically forbidden region to the left of the potential well and so we must set $x_0 = 0$ and use the exact boundary conditions.

The inward integration is done first and stopped at the grid point x_M where the relation

$$y_r(x_M) \geq 0$$

first occurs. This is our choice for the matching point x_M .¹⁷ The reason for this choice will become clear later in the discussion. The outward integration from x_0 to x_M is then carried out. At x_M we have calculated a "left" value, $y_l(x_M)$, and a "right" value $y_r(x_M)$ of the log derivative

function. These two quantities are equal only when the energy parameter E is equal to an eigenvalue. The difference

$$D(E) = c[y_r(x_M) - y_l(x_M)], \quad (10)$$

is a function of E . (The factor c is a constant that will be specified later.) Within some energy interval around an eigenvalue, $D(E)$ is a well behaved function of E that is zero at the eigenvalue and has a positive slope. An analytically derived example of $D(E)$ will be given later. For now it is sufficient to say that $D(E)$ is qualitatively similar in shape to a tangent function with roots at the eigenvalues and a pole between adjacent roots. It is somewhat analogous to the function $F(E)$ defined by Cooley.¹ The poles of $D(E)$ serve as boundary points that divide the energy axis into intervals. Within each interval, $D(E)$ is a monotonically increasing function with a single root. As a matter of convenient nomenclature, we refer to the energy interval which contains the n 'th eigenvalue as the n 'th interval and to the portion of the function $D(E)$ contained in this interval as the n 'th segment of $D(E)$.

A specific eigenvalue E_n is calculated in a two part procedure. The first part of the procedure is the bisection method analogous to that described previously. The inward and outward integrations are calculated and the poles of $y_l(x)$ are counted [$y_r(x)$ has no poles]. If the number of poles is greater than n , the trial energy is too high, and, if less than n , it is too low. If the pole count is equal to n we calculate $D(E)$. If $D(E)$ is negative, the trial energy is below the eigenvalue, and, if positive it is above. If the trial energy is low, it replaces E_L , and, if it is high, it replaces E_H ; then a new trial energy is calculated using Eq. (6). This procedure is iterated until the node counts for both E_L and E_H are equal to n , which indicates that both these energies are within the n 'th energy interval. We then switch over to a fast converging numerical method to quickly locate the root of the n 'th segment of $D(E)$. We have used the secant method¹⁸ for this; it is easy to program and has a quite adequate convergence rate. As a precaution, the convergence of the secant method is monitored, and, if it

starts to diverge, the program returns to the bisection procedure for two more iterations before trying the secant method again.

In order to obtain a better understanding of this log derivative formulation, it is useful to examine a simple analytically solvable model problem. The simplest bound-state problem is the infinite square well. The potential is zero in the interval from $0 \leq x \leq a$ and infinite elsewhere. The inward and outward solutions of Eq. (8), which obey the proper boundary conditions, are

$$y_r(x) = k \cot[k(x-a)] \quad (11)$$

and

$$y_i(x) = k \cot[kx] \quad (12)$$

where

$$k = (2\mu E)^{1/2}/\hbar \quad (13)$$

The matching point is defined by Eq. (9) where we can use the equality in this expression since an analytic solution is not restricted to grid points. Solve for this point, substitute into Eqs. (11) and (12), and then use Eq. (10) to obtain

$$D(E) = c \tan(ka) \quad (14)$$

The roots of this function occur at the energy values

$$E_n = (\pi^2 \hbar^2 / 2\mu a^2) n^2 \quad n = 1, 2, 3, \dots \quad (15)$$

which are obviously the eigenvalues of the infinite square well problem. ¹⁶

The function $D(E)$ has all the properties described earlier. The roots of $D(E)$ are fairly well centered within their respective energy intervals. This would not be the case if the matching point for the inward and outward integrations had been chosen differently. Let us assume that this point has some arbitrary value x_a . Then the function $D(E)$ would be

$$D(E) = c k \sin[ka] / \{\sin[k(x_a - a)] \sin[kx_a]\}. \quad (16)$$

It is clear that the roots of this function are still given by Eq. (15); however, the poles, which define the boundaries of the energy intervals, are changed depending on the value of x_a . A bad situation occurs if an interval boundary is very close to a root. This will increase the number of bisection iterations required to establish suitable upper and lower bounds before the secant method can be used. In the extreme case where the root and interval boundary coincide, the method would fail completely.

This reformulation in terms of the log derivative would just be an academic exercise if an efficient numerical method for solving Eq. (8) did not exist. Fortunately, such an algorithm is available.¹⁵ For convenience, we briefly restate it here and also derive the formula for integrating in the negative direction (inward integration). The outward integration formula is

$$y_n = (1 + h y_{n-1})^{-1} y_{n-1} - (h/3) w_n u_n, \quad (17)$$

where h is the spacing between the $M + 1$ grid points x_0, x_1, \dots, x_M and

$$u_n = \begin{cases} Q(x_n) & n = 0, 2, 4, \dots, M \\ [1 + (h^2/6)Q(x_n)]^{-1} Q(x_n) & n = 1, 3, 5, \dots, M-1. \end{cases} \quad (18)$$

The integration weight factors, w_n , are the same as in the Simpson integration rule, i.e.,

$$w_n = \begin{cases} 1 & n = 0, M \\ 4 & n = 1, 3, 5, \dots, M-1 \\ 2 & n = 2, 4, \dots, M-2 \end{cases} \quad (19)$$

Just as in a Simpson integration, the total number of grid points must be odd, therefore M must be an even integer. The quantity y_n is a good approximation to the log derivative $y(x_n)$ only at the final integration point $n = M$ where the weight factor is $w_M = 1$. We can save one multiplication per step by solving for the quantity $z_n = hy_n$. Multiplying Eq. (17) by h gives

$$z_n = (1 + z_{n-1})^{-1} z_{n-1} - (h^2/3) w_n u_n. \quad (20)$$

The log derivative at x_M can then be calculated in a final calculation

$$y_l(x_M) = h^{-1} z_M.$$

In order to calculate z_n using Eq. (20) we must know the initial term z_0 . This is related to the initial value of the log derivative, $y_l(x_0)$, by the formula

$$z_0 = h[y_l(x_0) - (h/3)Q(x_0)]. \quad (22)$$

We previously specified the initial value to be $y_l(x_0) = \infty$. Therefore, assuming $Q(x_0) < +\infty$; $z_0 = \infty$. (The special s-state, attractive Coulomb potential case can be calculated by a limiting procedure as $x \rightarrow 0$, and it can be shown that for reasonable values of h , we also obtain $z_0 = \infty$ at $x_0 = 0$.)

In order to count the poles of the log derivative function, we need a way to detect them. This turns out to be simple with the present algorithm. It is evident from the recurrence relation Eq. (20) that z_n is a fairly smooth function of the index n until a critical point is reached where $z_n < -1$. At the next grid point z_n has a positive value. This is the discontinuity of the log derivative function which occurs at the pole. Therefore, poles can be counted by the simple procedure of counting the number of times the situation $z_n < -1$ is encountered.

The "inward integration" recursion formula can be obtained by changing the sign of h and also changing $n-1$ to $n+1$ in Eq. (17). From this, we obtain the formula for $z_n = h y_n$

$$z_n = (1 - z_{n+1})^{-1} z_{n+1} + (h^2/3) w_n u_n. \quad (23)$$

The initial term for this inward integration is z_N . It is related to the log derivative, $y_r(x_N)$, by the formula

$$z_N = h[y_r(x_N) + (h/3)Q(x_N)]. \quad (24)$$

We previously specified this boundary value to be $y_r(x_N) = -\infty$. Thus, assuming $Q(x_N)$ is finite, $z_N = -\infty$. Just as in the outward integration formula, the total number of grid points must be an odd integer. Since M is an even valued integer, it follows that N is also an even valued integer. The weight factors are

$$w_n = \begin{cases} 1 & n = N, M \\ 4 & n = N-1, N-3, \dots, M+1 \\ 2 & n = N-2, N-4, \dots, M+2 \end{cases} \quad (25)$$

The result of doing the inward and outward integrations is a "right" value $z_r(x_M)$ and a "left" value $z_l(x_M)$, from which we calculate the difference function $D(E)$ [see Eq. (10)]

$$D(E) = z_r(x_M) - z_l(x_M). \quad (26)$$

The constant c in Eq. (10) has been set equal to h .

In an actual calculation we do not know the matching point x_M before hand. It is determined by doing the inward integration and monitoring the value of z_n at the even subscripted points. When the condition $z_n \geq 0$ (n = even integer) first occurs [see Eq. (9)], the integration is stopped and this point is, by definition, x_M . We find it convenient in the calculation to let the weight factor at x_M be the same as at any other even subscripted point i.e., $w_M = 2$ instead of $w_M = 1$, which is appropriate for an end point. A correction for this will be added later. The outward integration is done next with the weight factor at x_M also set to $w_M = 2$. The difference function is then calculated with the correction for using the wrong weight factors at x_M added as the third term on the right hand side

$$D(E) = z_r(x_M) - z_l(x_M) - 2(h^2/3)Q(x_M) \quad (27)$$

If the end points x_0 and x_N are located far enough inside the classically forbidden regions, the initial values z_0 and z_N are immaterial since any error rapidly decays to insignificance as the integration progresses through the forbidden regions. Under certain conditions, however, it is desirable to reduce the initial error as much as possible. An example of such a situation is when the eigenvalue is very close to the top of the potential well. In this case the error decays slowly as we integrate through the classically forbidden region. By using a good initial estimate, the interval of integration required for the error to become insignificant is reduced, thus, saving computer time. One method of calculating good estimates of

the initial values is by the W. K. B. approximation. The W. K. B. solution is obtained by neglecting the derivative term in Eq. (8). The resulting W. K. B. initial values are

$$y_l(x_0) = [-Q(x_0)]^{1/2} \quad (28)$$

and

$$y_r(x_N) = -[-Q(x_N)]^{1/2}. \quad (29)$$

The appropriate values for x_0 and x_N are obtained by substituting these values into Eqs. (22) and (24), respectively.

B. The Renormalized Numerov Method

The Numerov method is an efficient algorithm that can be used to obtain numerical solutions of Eq. (1).¹⁹ The basic formula is the three term recurrence relation

$$[1 - T_{n+1}]\phi_{n+1} - [2 + 10T_n]\phi_n + [1 - T_{n-1}]\phi_{n-1} = 0 \quad (30)$$

where

$$\phi_n = \psi(x_n) \quad (31)$$

and

$$T_n = -(h^2/12)Q(x_n) \quad (32)$$

Here h is the spacing between the grid points and $Q(x)$ is defined by Eq (2).

The renormalized Numerov algorithm is derived from Eq. (30) by making two transformations. The first transformation²⁰ consists of defining the quantity

$$F_n = [1 - T_n]\phi_n, \quad (33)$$

and substituting into Eq. (30). This gives

$$F_{n+1} - U_n F_n + F_{n-1} = 0 \quad (34)$$

where

$$U_n = (1 - T_n)^{-1}(2 + 10T_n). \quad (35)$$

The advantage of this transformation is that one less multiplication per step is necessary to calculate F_n than ϕ_n . The next transformation is commonly used to replace a three point recurrence relation with a two point relation.²¹ Define the ratio

$$R_n = F_{n+1}/F_n. \quad (36)$$

Substitute this into Eq. (34) to obtain the two term recurrence relation

$$R_n = U_n - R_{n-1}^{-1}. \quad (37)$$

R_n can also be expressed as a continued fraction

$$R_n = U_n - \frac{1}{U_{n-1}} - \frac{1}{U_{n-2}} - \dots - \frac{1}{U_1} - R_0 \quad (38)$$

The quantity R_n is useful as we will soon show. We prefer to calculate it instead of F_n because, unlike this quantity, it does not grow exponentially in the classically forbidden regions.

Equation (37) is calculated once the initial value R_0 is specified. The value that corresponds to the conditions $\psi(x_0) = 0$ and $\psi(x_1) \neq 0$ is $R_0 = \infty$. If the iteration is stopped at any point x_n , the quantities R_n and R_{n-1}^{-1} are immediately available with no additional calculations. From these quantities and using Eqs. (36) and (33), we can calculate the wavefunction at the points x_{n+1} , x_n , and x_{n-1} to within a normalization factor N ;

$$\psi_{n+1} = N(1 - T_{n+1})^{-1} R_n \quad (39)$$

$$\psi_n = N(1 - T_n)^{-1} \quad (40)$$

$$\psi_{n-1} = N(1 - T_{n-1})^{-1} R_{n-1}^{-1} \quad (41)$$

In this sense, we are calculating a renormalized wavefunction at each step. This is the origin of the designation "renormalized Numerov" method.

Blatt⁴ has derived a formula for computing the derivative of the wavefunction at the point x_n .

$$\psi_n' = h^{-1} [(1/2 - T_{n+1}) \psi_{n+1} - (1/2 - T_{n-1}) \psi_{n-1}] \quad (42)$$

The error term, which is neglected in the derivation of this formula, is of order h^5 , which is poorer than the order h^6 error of the basic Numerov formula. Because of this, Blatt⁴ also derived another slightly more

complicated formula for the derivative in which the error term is of order h^9 . Sloan,²² however, has shown that the cumulative error of the Numerov method at a fixed value of x is of order h^4 . Therefore, it appears that Eq. (42) should probably give all the accuracy possible and nothing would be gained by using the 9'th order formula. We tested both methods numerically on a simple problem and found this to be the case. Initially, for the first few iterations, the 9'th order method gave much more accurate results than Eq. (42). However, after integrating over only a small interval, the cumulative error in the Numerov calculated wavefunction built up and from then on the size of the errors in the derivatives was about the same for both formulas. Therefore, we conclude that the simpler formula, Eq. (42), gives all the accuracy possible and we use it.

The derivative of the wavefunction at the point x_n can be calculated to within the normalization factor N by substituting Eqs. (39) and (41) into Eq. (42). Then divide this by the wavefunction ψ_n given by Eq. (40) to obtain the log derivative at x_n [see Eq. (7)]. The normalization factor N cancels in the numerator, and denominator and the result is

$$y_l(x_n) = h^{-1} [A_{n+1} R_n - A_{n-1} R_{n-1}^{-1}] (1 - T_n) \quad (43)$$

where

$$A_n = (1/2 - T_n)(1 - T_n)^{-1} \quad (44)$$

Although we are only considering single channel bound state problems in this report, it is worth mentioning that the renormalized Numerov formulas are easily generalised to a multichannel matrix formulation. In particular Eq. (43) generalises to give the log derivative matrix from which the scattering matrix can be computed.

Equation (34) can be iterated in the reverse direction (i.e., decreasing index n) as well as the forward direction. For the reverse iteration it is convenient to redefine the ratio [see Eq. (36)]

$$\tilde{R}_n = F_{n-1}/F_n. \quad (45)$$

where the tilde is used to distinguish this ratio from the ratio [Eq. (36)] used for the forward iteration. Substituting this into Eq. (34), we obtain the two term recurrence formula

$$\tilde{R}_n = U_n - \tilde{R}_{n+1}^{-1}. \quad (46)$$

This formula can be iterated once the initial value \tilde{R}_N is specified. The value that corresponds to $\phi(x_N) = 0$ and $\phi(x_{N-1}) \neq 0$ is $\tilde{R}_N = \infty$. The derivation of the formula for the log derivative $y_r(x_n)$ is similar to the derivation of Eq. (43). The result is

$$y_r(x_n) = h^{-1} [A_{n+1} \tilde{R}_{n+1}^{-1} - A_{n-1} \tilde{R}_n] (1 - T_n), \quad (47)$$

where A_n is defined by Eq. (44). As the inward iteration of Eq. (46) proceeds, the value of the ratio \tilde{R}_n is monitored. When the condition $\tilde{R}_n \leq 1$ first occurs, the iteration is stopped and this point is, by definition, the matching point x_M . This is approximately the position where the first derivative of the wavefunction is zero, which is the same condition implied by Eq. (9). The outward iteration from x_0 to x_M is carried out next. During this calculation, the nodes of the wavefunction are counted. A node located between x_n and x_{n+1} will give rise to the condition $R_n < 0$. Thus, in order to count the number of nodes in the interval from x_0 to x_M , we monitor R_n from $1 \leq n \leq M-1$ and count the number of times it is negative. The function $D(E)$ is computed by substituting Eqs. (43) and (47) into Eq. (10) with $c = h$.

$$D(E) = [A_{M+1}(\tilde{R}_{M+1}^{-1} - R_M) - A_{M-1}(\tilde{R}_M - R_{M-1}^{-1})](1 - T_M). \quad (48)$$

The procedure outlined above will be referred to as method A. A slight variation of this procedure, to be referred to as method B, will be described next. The only difference between the two methods is the way in which the function $D(E)$ is calculated. From the definitions of R_n and \tilde{R}_n given by Eqs. (36) and (45), respectively, it is obvious that the equality $R_M = \tilde{R}_{M+1}^{-1}$ is true only if E is an eigenvalue. It follows that the function²³

$$\tilde{D}(E) = \tilde{R}_{M+1}^{-1} - R_M \quad (49)$$

is zero at the eigenvalues. With a little thought, one can also be convinced that the slope is positive at the root. Although this function is not equal to the one defined by Eq. (48), it is very similar in shape and has all the properties required for the calculation of the eigenvalues. In fact, it can be shown that the two functions differ from each other only by a term of order h^2 . This follows from Eqs. (32), (33), (36), and (45), from which we obtain

$$R_n = 1 + hy_f(x_n) + O(h^2) \quad (50)$$

and

$$\tilde{R}_{n+1}^{-1} = 1 + hy_f(x_n) + O(h^2). \quad (51)$$

Substituting these into Eq. (49) and using Eq. (10) with $c = h$ gives²⁴

$$\tilde{D}(E) = D(E) + O(h^2). \quad (52)$$

Methods A and B seem to work equally well. Method B has the advantage that it is slightly easier to program the calculation of Eq. (49) than Eq. (48).

III. EIGENFUNCTIONS

In this section we describe the renormalized Numerov method for computing the eigenfunctions and also derive a useful interpolation formula.

It is assumed that the eigenvalue has already been calculated. With the energy parameter set equal to this eigenvalue, Eq. (37) is solved for the values of R_1, R_2, \dots, R_M and Eq. (46) is solved for $\tilde{R}_{N-1}, \tilde{R}_{N-2}, \dots, \tilde{R}_M$. (These quantities do not need to be recomputed if they are saved from the eigenvalue calculation.) The next step is to calculate F_n . Since the normalization of the wavefunction is arbitrary, let $F_M = 1$. The values of F_n for $n < M$ are calculated iteratively using Eq. (36), and the values for $n > M$ are calculated using Eq. (45). The value of the wavefunction at each point can then be computed using Eq. (33).²⁵ One advantage this procedure has over a direct integration of the Numerov formula, Eq. (30), is that we avoid any computer overflow problems that could arise due to the exponentially increasing nature of the solution in the classically forbidden regions.

For some problems it is necessary to know the value of the wavefunction at points other than the evenly spaced grid points. For example, if we want to integrate some expression containing the wavefunction, such as a matrix element or Franck Condon factor, by Gauss quadrature, the wavefunction must be known at the appropriate Gauss points. For these problems it is useful to have a simple interpolation formula that will allow the calculation of the wavefunction at an arbitrary point to the same accuracy as it is known at the grid points. Such a formula can be derived by reasoning similar to that used to derive the Numerov formula.

Assume that we want to compute the value of the wavefunction at a point x_α which is between the two grid points x_{l-1} and x_l

$$x_l = x_\alpha + (1 - \alpha)h \quad (53)$$

$$x_{l-1} = x_\alpha - \alpha h \quad (54)$$

where

$$h = x_i - x_{i-1} \text{ and } 0 \leq \alpha \leq 1. \quad (55)$$

For convenience, define

$$\beta = (1 - \alpha), \quad (56)$$

Make a Taylor expansion of the wavefunction around the point x_α :

$$\phi_i = \phi_\alpha + \beta h \phi'_\alpha + (\beta^2 h^2 / 2) \phi''_\alpha + (\beta^3 h^3 / 6) \phi'''_\alpha + O(h^4) \phi''''_\alpha, \quad (57)$$

$$\phi_{i-1} = \phi_\alpha - \alpha h \phi'_\alpha + (\alpha^2 h^2 / 2) \phi''_\alpha - (\alpha^3 h^3 / 6) \phi'''_\alpha + O(h^4) \phi''''_\alpha. \quad (58)$$

Here $O(h^4)$ represents a term of order h^4 . Multiply Eq. (57) by β^{-1} and Eq. (58) by α^{-1} and add

$$\beta^{-1} \phi_i + \alpha^{-1} \phi_{i-1} = (\alpha\beta)^{-1} \phi_\alpha + (h^2 / 2) \phi''_\alpha + (\beta - \alpha)(h^3 / 6) \phi'''_\alpha + O(h^4) \phi''''_\alpha. \quad (59)$$

Differentiate Eqs. (57) and (58) twice, add the resulting equations and multiply by $h^2 / 6$ to obtain

$$(h^2 / 6) [\phi''_i + \phi''_{i-1}] = (h^2 / 3) \phi''_\alpha + (\beta - \alpha)(h^3 / 6) \phi'''_\alpha + O(h^4) \phi''''_\alpha. \quad (60)$$

Subtract this from Eq. (59) to obtain

$$[\beta^{-1} \phi_i + \alpha^{-1} \phi_{i-1}] - (h^2 / 6) [\phi''_i + \phi''_{i-1}] = (\alpha\beta)^{-1} \phi_\alpha + (h^2 / 6) \phi''_\alpha + O(h^4) \phi''''_\alpha, \quad (61)$$

then use the Schrodinger equation to eliminate the second derivative terms. The final expression for the interpolation formula is

$$\psi_{\alpha} = [(\alpha\beta)^{-1} + \gamma_{\alpha}]^{-1} \{(\beta^{-1} - \gamma_i)\psi_i + (\alpha^{-1} - \gamma_{i-1})\psi_{i-1}\}, \quad (62)$$

where

$$\gamma_n = -(h^2/6)Q(x_n). \quad (63)$$

The truncation error for this formula is of order h^4 , which is the same as the cumulative error at a fixed value of x of the Numerov formula.²² We have verified by numerical calculations on an example problem that no precision is lost using this formula. The value of the wavefunction at the interpolated points is just as accurate, on the average, as it is at the grid points.

IV. EXAMPLE CALCULATIONS AND DISCUSSION

Computer programs employing all the methods described in the preceding sections have been written and used to solve a variety of problems. Some results of three test cases are presented and discussed in this section. All results were obtained using the Aerospace CDC 7600 computer and Fortran codes.

The first two example calculations are the Morse potential problem and the unsymmetrical double minimum potential problem that were discussed by Wicke and Harris.⁶ The functional form for both potentials is given by

$$V(x) = D\{1 - \exp[-B(x - x_a)]\}^2 + A\exp[-C(x - x_b)^2], \quad (64)$$

where the parameter A is zero for the Morse problem. The potential parameters and reduced mass are given in Table I of Ref. (6) and also here in Table I. The integration limits for all calculations on both problems were $x_{\min} = 1.0\text{\AA}$ and $x_{\max} = 2.6\text{\AA}$.

Results for the Morse problem are given in Table II. They are presented as the difference between the numerically calculated eigenvalues and the analytic eigenvalues calculated from the formula²⁶

$$E_n = 1000(n + 1/2) - 8(n + 1/2)^2. \quad (65)$$

The renormalized Numerov²⁷ (RN) calculation was done with 2049 grid points and required about 0.73 seconds. The log derivative (LD) method requires fewer computer operations per grid point than the RN, but requires more points to achieve the same accuracy. These two effects almost compensate, making the total computation time about the same. The LD results in Table II were calculated with 2617 points; the time required was 0.75 seconds. Calculations to this degree of accuracy can

Table I. Potential Parameters (Taken from Table I in Ref. 6)

Computer programs employing all the methods described in the preceding sections have been written and used to solve a variety of problems. Some results of these test cases are presented and discussed in this section.

The first two examples considered are the Morse potential problem and the unsymmetrical double minimum potential problem that were discussed by Wicks and Wicks (1964) and given by

$$D = 31250 \text{ cm}^{-1}$$

$$B = (8\pi^2 c \mu \omega_e x_e / h)^{1/2} \times 10^{-8} \text{ Å}^{-1}$$

$$x_a = 1.5 \text{ Å}$$

$$\omega_e = 1000 \text{ cm}^{-1}$$

$$\omega_e x_e = 8 \text{ cm}^{-1}$$

$$\mu = 5 \text{ g/mole}$$

$$A = 10,000 \text{ cm}^{-1}$$

$$C = 200 \text{ Å}^{-2}$$

$$x_b = 1.6 \text{ Å}$$

Table II. Differences between Numerical and Analytic Results for the Morse Potential Problem; $E_n^{\text{numerical}} - E_n^{\text{analytic}}$ (cm^{-1}) Multiplied by 10^7 .

n	E_n^{analytic}	Renormalized Numerov ^a	Log Derivative ^b	Richardson Extrapolation ^c
0	498	1	0	-0
1	1482	2	2	-0
2	2450	8	7	-2
3	3402	18	18	-5
4	4338	35	35	-13
5	5258	61	61	-26
6	6162	95	95	-46
7	7050	139	139	-77
8	7922	194	194	-119
9	8778	259	259	-175
10	9618	334	334	-247
11	10442	420	421	-337
12	11250	516	517	-445
13	12042	622	623	-573
14	12818	737	738	-722
15	13578	860	862	-892

^aCalculated with 2049 integration points. $T = 0.73$ seconds.

^bCalculated with 2617 integration points. $T = 0.75$ seconds.

^cExtrapolated from renormalized Numerov calculations using 261 and 521 integration points. $T = 0.2$ seconds.

be done more economically by using the Richardson extrapolation technique.^{28, 18} It has been verified by numerical calculations that the truncation error for both the RN and LD methods is given by

$$E_n^{\text{calc}} - E_n^{\text{exact}} = C_4 h^4 + C_6 h^6 + \dots \quad (66)$$

where h is the grid spacing. This formula is used to extrapolate the eigenvalues calculated using several different values of h to $h = 0$. Results of extrapolation of RN calculations using 261 and 521 grid points are given in Table II. The total time required for this calculation was 0.2 seconds. Since some integration methods discussed in the literature require good initial estimates of the eigenvalues,^{1, 3, 6} it should be emphasized that no such initial estimates were required or used in these calculations.

A portion of the function $D(E)$, calculated for the Morse problem by the renormalized Numerov method A, is shown in Fig. 1. All of the $n = 2$ segment and parts of the adjacent $n = 1$ and $n = 3$ segments are plotted. The vertical bars at $E = 1920 \text{ cm}^{-1}$ and $E = 2880 \text{ cm}^{-1}$ are the lower and upper boundaries of the second energy interval.

Results for the unsymmetric double minimum potential problem are given in Table III. This calculation was done by the renormalized Numerov method using 2049 points. The time required was 0.86 seconds. These values differ by a small, but significant, amount from those obtained by Wicke and Harris [see Table II in Ref. (6)]. Because of this difference we checked our results by doing an independent calculation with a basis function expansion method utilizing a 60 term harmonic oscillator function expansion. The agreement was excellent, convincing us that the results in Table III are correct. The difference between our results and those of Wicke and Harris is probably due to differences in the calculated values of the Morse parameter B and the factor $\hbar^2/2\mu$ used in the respective calculations. In order to be unambiguous about the model problem we are solving, we give our value of B to 14 decimal digits;²⁹ $B = 1.5403756164035$. The factor $\hbar^2/2\mu$ was calculated by using the formula³⁰ $\hbar^2/2\mu = 6/B^2$.

Table III. Eigenvalues for the Unsymmetric and Symmetric Double Minimum Potential Problems
Calculated using the Renormalized Numerov Method A.

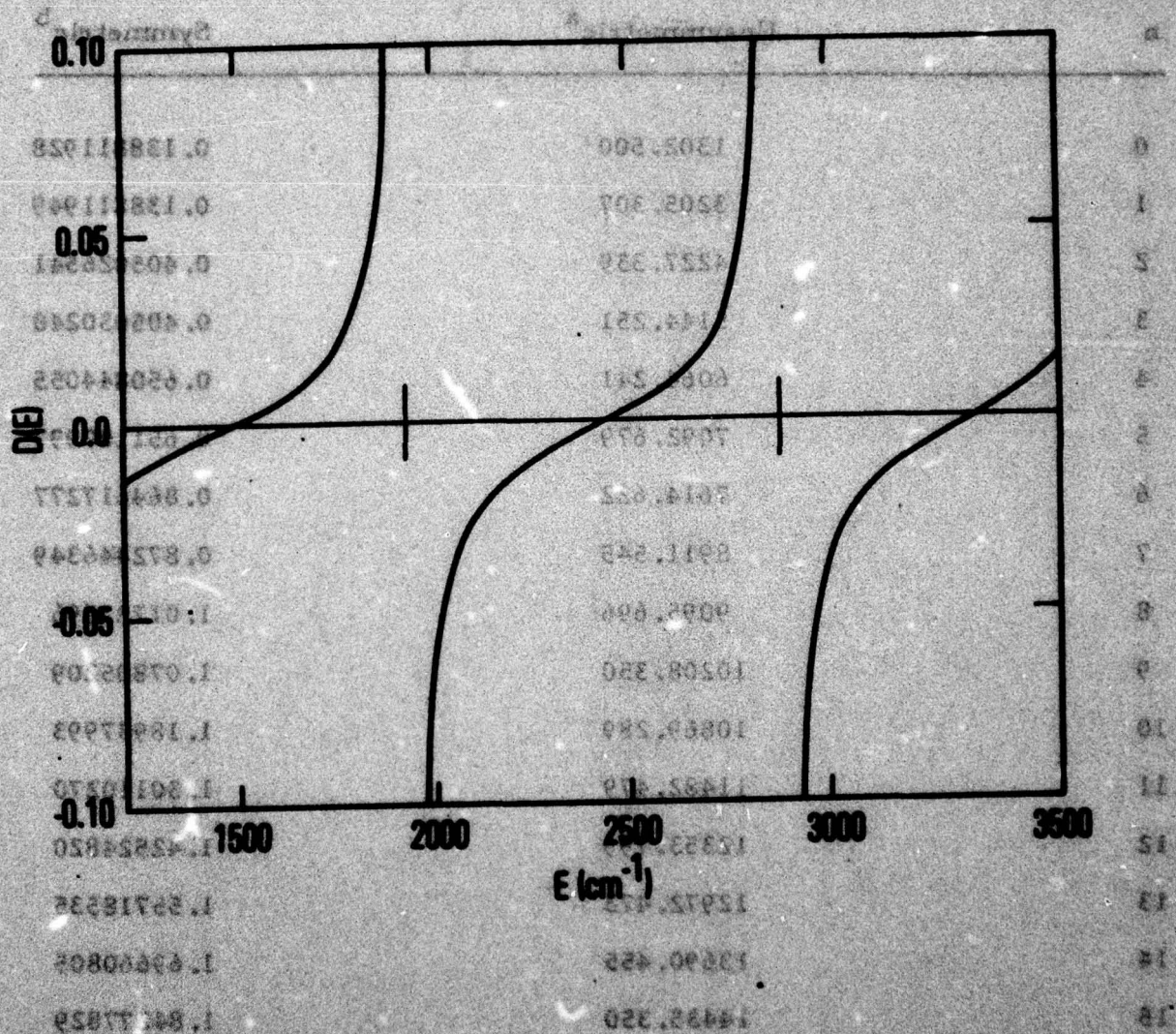


Figure 1. The Function $D(E)$ Calculated by the Renormalized Numerov Method A for the Morse Potential Problem. The Three Roots are the $n = 1, 2$ and 3 Eigenvalues.

**Table III. Eigenvalues for the Unsymmetric and Symmetric
Double Minimum Potential Problems
Calculated using the Renormalized Numerov Method A.**

n	Unsymmetric ^a	Symmetric ^b
0	1302.500	0.138811928
1	3205.307	0.138811949
2	4227.339	0.405026541
3	5144.251	0.405030240
4	6064.241	0.650844055
5	7092.679	0.651100997
6	7614.622	0.864617277
7	8911.545	0.872446349
8	9095.696	1.01722896
9	10208.350	1.07805209
10	10869.289	1.18937993
11	11482.479	1.30110270
12	12353.799	1.42524820
13	12972.473	1.55718535
14	13690.455	1.69660805
15	14435.350	1.84277829

^aExpressed in cm⁻¹ units.

^bExpressed in same arbitrary units as the potential.

The function $D(E)$ was computed for this problem, and it was observed that the third energy interval is very narrow. The lower boundary is located at $E = 5097 \text{ cm}^{-1}$, and the upper boundary is at $E = 5145 \text{ cm}^{-1}$. Because this interval is so narrow, more bisection iterations than usual are required before we switch over to the fast converging secant method. The small width is due to the condition that the matching point x_M is located near the outer minimum while the $n = 3$ eigenfunction is mainly localized around the inner minimum. In order to demonstrate this, we altered the program so that the matching point was located near the inner minimum. In this case the third energy interval was much wider with the lower boundary at $E = 4230 \text{ cm}^{-1}$ and the upper boundary at $E = 6030 \text{ cm}^{-1}$. A more sophisticated program could be written, which would automatically locate the matching point in the region where the wavefunction is mainly localized; however, we did not do this. It should be emphasized that no matter how narrow an interval is, our procedure never fails to converge to the desired eigenvalue; it simply requires a few more bisection iterations. This is the reason that the double minimum problem required slightly more time to solve than the Morse problem. In a more extreme test case we changed the Gaussian amplitude factor in the potential to $A = 20000$. In this case the $n = 3$ energy interval was so extremely narrow that convergence was achieved entirely by the bisection method; the secant method was never called into use.

(20) The third example calculation is a symmetric double minimum potential problem. The potential, in arbitrary units, is

$$V(x) = (x^2 - 1)^2. \quad (67)$$

and in the same units $\hbar^2/2\mu = 0.005$. This completely defines the model problem. The lowest 16 eigenvalues, calculated by the renormalized Numerov method A, are given in Table III. The integration limits were ± 2.0 , the number of grid points was 4001, and the time required was 1.9 seconds. Since the lower eigenvalues are doublets with very small

splittings, the convergence to these values will be almost entirely by the bisection procedure. This fact in conjunction with the large number of integration points accounts for the increased time to solve this problem.

Another method, which takes account of the symmetry, can be used to solve this problem more efficiently. The integration is carried out over only half the range, $x_{\min} = 0$ to $x_{\max} = 2$, and the symmetric and antisymmetric solutions are obtained in separate calculations. This method is more efficient for two reasons: The integration covers only half the range, and since the eigenvalues no longer appear as doublets, fewer iterations by the bisection method are required. The antisymmetric eigenfunctions are calculated by merely changing the starting point of the outward integration from $x_0 = -2$ to $x_0 = 0$. Since the wavefunction is zero at this point, the inner boundary condition is the same as we have discussed previously. The symmetric wavefunctions, on the other hand, have zero slope at $x = 0$. From this we obtain $y_1(x_0) = 0$, which is substituted into Eq. (22) to calculate the initial term z_0 of the log derivative solution. The initial term, R_0 , of a renormalized Numerov solution is also easy to derive. Let ϕ_{-1} , ϕ_0 , and ϕ_1 be the values of the wavefunction at the grid points $x_{-1} = -h$, $x_0 = 0$, and $x_1 = h$. From symmetry it follows that $\phi_{-1} = \phi_1$ and also $F_{-1} = F_1$. Substituting this into Eq. (34) and using Eq. (36) we obtain the desired initial term

$$R_0 = U_0/2, \quad (68)$$

where U_0 is defined by Eq. (35).

A calculation of the symmetric and antisymmetric solutions was calculated this way using the renormalized Numerov method. The results are exactly the same as obtained previously and listed in Table III. The number of grid points used was 2001 and the total time required to calculate the 16 eigenvalues was 0.5 seconds.

We have compared the three methods used here, i.e., the log derivative and the renormalised Numerov methods A and B, to try and determine their relative merits for ease of programming and computational efficiency. The differences are only slight. However, based on these very small differences, we would recommend the renormalised Numerov method B as the easiest to program and the most efficient of computer time.

FOOTNOTES AND REFERENCES

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24. The reader is reminded that the quantity $D(E)$ in Eq. (52) is of order h so the term $O(h^2)$ is only one order of h smaller in magnitude.
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